A New Synthesis of Octafluoro[2.2]paracyclophane

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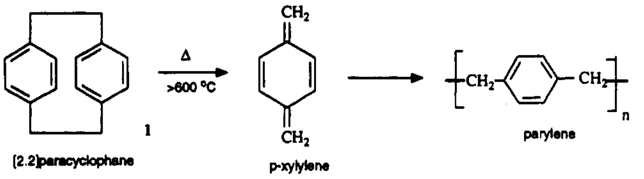
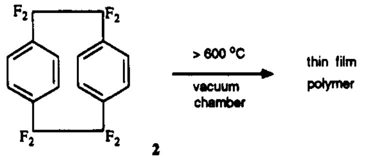
A new synthesis of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (2) is reported. Easy preparation of gram quantities of 2 is accomplished by treatment of α,α'-dibromo-$\alpha,\alpha,\alpha',\alpha'$-tetrafluoroxylene with a complex low-valent form of Ti which is made by reduction of $TiCl_4$ with equimolar quantities of $LiAlH_4$ in THF. Use of high-dilution techniques is required for the reaction to be successful. The formation of 2 is believed to proceed via the reactive monomeric species $\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylylene (4).

The first report of a [2.2]paracyclophane resulted from the isolation of the parent species 1 from a polymer mixture in 1949.[1] However the development of cyclophane chemistry as a field of research was due to the pioneering work of Cram and his co-workers. His first publication of a designed synthesis of 1 appeared in 1951.[2] From the beginnning it was apparent that the [2.2]paracyclophanes would be valuable compounds for testing theories of bonding, ring strain, and π-electron interactions. Certainly the breadth and scope of developments in this field bear out these early expectations.[3,4] Spectroscopic effects resulting from transannular electronic effects, torsional chirality resulting from restricted rotation of the rings, and transannular influences in electrophilic substitution reactions all gave rise to early interest in such systems. More recently [2.2]paracyclophanes have been used to create unique spherand-type "host" molecules,[5] while the organometallic chemistry of these molecules gives evidence of being a very rich field.[3]

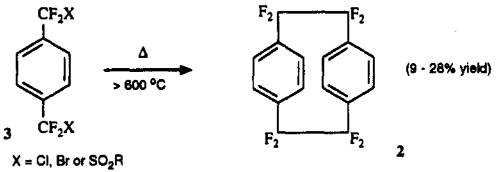


In addition it has long been recognized that [2.2]-paracyclophanes are useful precursors of thin film polymers, known in the industry as "parylenes".[6] Such parylenes are ideally suited for use as conformal coatings in a wide variety of fields such as in the electronics, automotive, and medical industries. Parylene coatings are inert and transparent and have excellent barrier properties. The parylene generated from the parent hydrocarbon 1 has been found to be useful at temperatures up to 130 °C.[6]

Octafluoro[2.2]paracyclophane (2), a bridge-fluorinated version of 1 and known in the industry as AF4, also provides an inert, transparent conformal coating which should be particularly useful as a coating material which can withstand harsh environments such as exposure to weather, salt, corrosive chemicals, etc.[7] In addition, parylene made from 2 can tolerate temperatures as high as 240 °C, which makes it suitable for high-temperature applications such as the coating of electrical components used near automobile engines.


2

However, in spite of its potential commercial utility, 2 has not been extensively used as a parylene precursor because the only reported preparative methods for 2 involve pyrolysis of a precursor at temperatures >600 °C.[8]


3 2
AF4

The special apparatus required for the synthesis makes laboratory preparation unattractive, while the required high temperatures make commercialization impracticable.

We report in this paper a new, nonpyrolytic method for the synthesis of 2, one which allows easy laboratory preparation of gram quantities of 2 while nevertheless still presenting difficulties with regard to commercialization because of the high-dilution methodology which is required for good yields of high purity product.

Methods of synthesis of [2.2]paracyclophanes are quite diverse. Reviews of the various methodologies are available.[3,9,10] In our approach to new methods for the preparation of 2, we centered our attention on processes which involve generation and dimerization of the monomeric species $\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylylene (4). In principle, any method which could generate 4 would also be a potential source of 2. Unfortunately, 4 can alternatively simply polymerize to a virtually-useless form of the parylene polymer.

Until now, applications of all classical reduction methodologies to the reductive elimination of X_2 from 3 have

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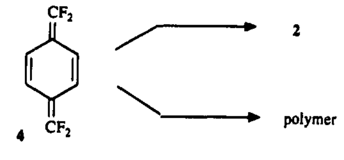
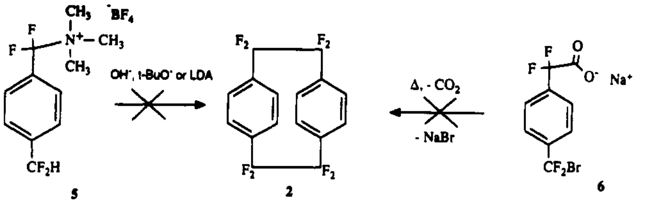


resulted in *only* formation of polymer. Methods which were attempted some 25 years ago include the use of Zn dust, Zn–Cu couple, BuLi, and electrochemical reduction.[11]

The currently favored method for preparing the parent [2.2[paracyclophane (1) utilizes a Hofmann elimination process.[12,13] Unfortunately we found that the analogous fluorinated precursor **5** did not undergo the desired Hofmann elimination process to form **2**.[14]

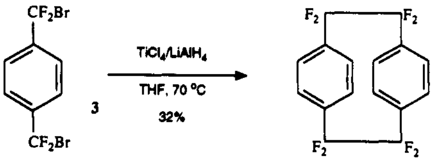


Another logical precursor to the monomeric **4** would be the carboxylic acid salt **6**.[14] However, attempted decarboxylative elimination of **6** to form **2** proved unsuccessful.

Indeed, in the end, a procedure involving reductive elimination from the readily obtained precursor **3** (X = Br) was discovered which led to the desired fluorinated paracyclophane **2** in a yield which was considered quite good for a [2.2]paracyclophane-forming reaction. Dibromide **3** was easily synthesized via a two-step procedure beginning with *p*-phthalaldehyde.[8,15]

After a number of unsuccessful attempts at productive reductive-elimination using sodium naphthylenide, magnesium, Zn(Cu), and Mg(Hg), a reduced form of Ti (hence referred to as Ti*), prepared by treatment of $TiCl_4$ with equimolar amounts of $LiAlH_4$ in THF, was tried as the reducing agent.[16-18] This reagent was chosen because of our prior experience in utilizing it to generate fluorochlorocarbene from $CFCl_3$ in THF,[19] and because it had been successfully used to couple benzyl halides,[20,21] and carry out 1,2-dehalogenations.[22] The reactive form of Ti from this method of formation likely has an average oxidation state of +1[23] and it exists as a *finely divided black suspension* in THF. When the reaction was carried out by slow addition of 0 °C of dilute **3** in THF to 3.6 equiv of a reducing medium formed by reacting equimolar quantities of $LiAlH_4$ and $TiCl_4$ in THF, **2** was formed in 18% yield.

Optimization of conditions led to the determination that 70 °C was the best temperature for the reaction and THF the best solvent, although dimethoxyethane and dioxane also worked. It was found that the yield and purity were highest when the reaction was carried out under conditions of *high dilution*. Thus, optimally, 1 g (3 mmol) of **3** in 450 mL of anhydrous THF was added, under an inert atmosphere, over a period of 12 h to a refluxing mixture of reduced titanium (formed from reaction of 2.05 g (10.8 mmol) $TiCl_4$ with 0.41 g (10.8 mmol) of $LiAlH_4$) in a total of 150 mL of anhydrous THF to form 0.17 g (0.48 mmol) of **2** (32% yield).



Indeed, GC yields could be increased to as high as 46% at the 1-g scale if one resorted to ultimate high dilution techniques, wherein *both* **3** and the suspension of reduced Ti were simultaneously and slowly added to a bath of refluxing THF. Working at 10-g scale, an *isolated* yield of 32% could be obtained using this method.

Other forms of Ti, including those formed from reductions of $TiCl_4$ by K, Mg, and $Li(C_2H_5)_3BH$, were found to be unsatisfactory in converting **3** to **2**.[24-26] Other metals such as Rieke Zn, Mg, Mn, Fe, and Cu, $CoCl_2/LiAlH_4$, and $VCl_3/LiAlH_4$ were found to be similarly ineffective.[27-33]

As of now, the only other reducing agent which was found to give as much as 10% yield of **2** from **3** was samarium diiodide.[34,35] When dibromide **3** was added slowly to a 5-fold excess of SmI_2 in THF at rt, yields of 22% **2** and 16% trimer were obtained.

Interestingly the Ti reagent appeared to work best for generation of the *fluorinated* [2.2]paracyclophane, and it also worked better for **3** (X = Br) than for **3** (X = Cl). When α,α'-dibromo-*p*-xylene was treated with the $TiCl_4/LiAlH_4$ reagent, the highest observed yield for formation of the parent [2.2]paracyclophane (**1**) was 20–21%. Likewise when dichloro precursor **3** (X = Cl) is used in place of the *dibromide*, only a 22% yield of **2** is obtained.

In separate control reactions, **2** was found to be stable to the reaction conditions but highly reactive with $LiAlH_4$/THF, with efficient conversion to the reduced species, $\alpha,\alpha,\alpha',\alpha'$-tetrafluoroxylene, being observed.

Mechanism. It is believed that formation of **2** from **3** proceeds via the intermediacy of the monomer, $\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylylene, (**4**). Consistent with its intermediacy is the observation of small amounts of trimer in the product mixture, as detected by both ^{19}F NMR and GC/MS. Trimer amounts to but a small impurity when the reaction is carried out under ideal high-dilution conditions, but when such conditions are compromised in any way, the result is an increase in the formation of trimer.

The most likely alternative mechanism for dimer formation, namely that of sequential titanium-induced

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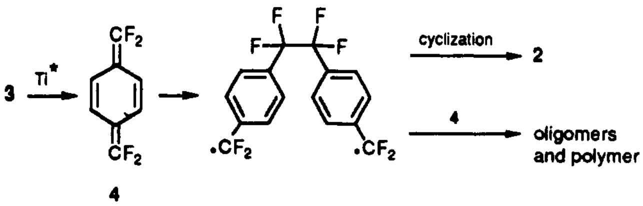
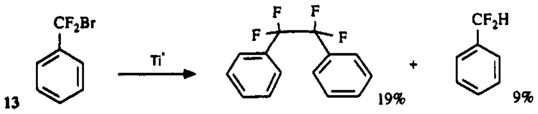


coupling via the half-coupled intermediate, 7 has been excluded. Potential intermediate 7 has been independently synthesized as shown in Scheme I, but could *not* be converted to 2 under the reaction conditions.

In light of the successful use of Ti* in coupling benzyl halides, the coupling of simple α,α-difluorobenzyl bromides, i.e. 13, was attempted, with little success.



Conclusions. It would this appear that when the appropriate reaction conditions are applied, dibromide 3 can be induced to undergo productive *reductive elimination* to form the reactive tetrafluoro-*p*-xylylene intermediate 4, which under conditions of high dilution can itself undergo dimerization to form octafluoro[2.2]paracyclophane (2). Thus far only *one* reducing agent, a complex, reduced form of titanium prepared from equimolar quantities of $TiCl_4$ and $LiAlH_4$ in THF, has been found effective for carrying out preparatively useful conversions of 3 to 2.

Experimental Section

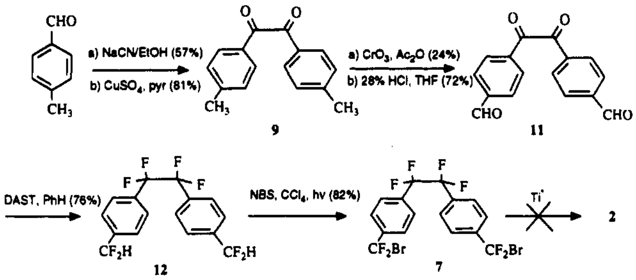
NMR spectra were measured in $CDCl_3$ as solvent unless otherwise noted, and $CFCl_3$ was used as the ^{19}F internal standard. Boiling points were measured by Siwoloboff's method and are uncorrected.

***p*-Bis(bromodifluoromethyl)benzene (3)** was prepared by the method of Hasek,[36] which was improved by Fuqua[15] and Chow.[8] The reaction of terephthalaldehyde with SF_4 in an autoclave at 150 °C on a 0.15-mol scale led to a yield of 88% of *p*-bis(difluoromethyl)benzene: ^1H NMR δ 6.63 (t, J = 56.5 Hz, 2 H), 7.56 ppm (s, 4 H); ^{13}C NMR δ 114.2 (t, J = 237.7 Hz, CHF_2), 126.0 (t, J = 5.8 Hz), 136.8 ppm (t, J = 22.4 Hz); ^{19}F NMR ϕ −112.1 ppm (d, J = 56.5 Hz). Treatment of this product with 2.3 equiv of *N*-bromosuccinimide in CCl_4 under constant reflux and irradiation led to formation of 3 in 78% yield: bp 102–107 °C/25 mmHg; ^1H NMR δ 7.69 (ppm (s); ^{13}C NMR, δ 117.3 (t, J = 302.2 Hz, CF_2Br), 124.9 (t, J = 5 Hz), 140.7 ppm (t, J = 24.3 Hz): ^{19}F NMR ϕ −45.65 ppm (s).

***p*-Bis(Chlorodifluoromethyl)benzene** was prepared by the method of Chow,[8] with an 85% isolated yield being obtained in our hands: bp 59–60 °C/11 mmHg; ^1H NMR δ7.73 ppm (s); ^{13}C NMR δ 125.3 (t, J_{CF} = 4.9 Hz), 125.7 (t, J = 307.5 Hz, CF_2Cl), 139.2 (t, J_{CF} = 26.9 Hz); ^{19}F NMR ϕ −50.4 ppm.

Preparation of Octafluoro[2.2]paracyclophane (2) (Method A). To a stirred solution of 20.5 g (0.108 mol) of $TiCl_4$ in 500 mL of anhydrous THF under Ar was added slowly, with cooling by an ice bath, 4.1 g (0.108 mol) of $LiAlH_4$ in 200 mL of THF. As the $LiAlH_4$ was added, the mixture underwent a number of color changes, starting out as a yellow suspension, becoming green, and ending up as a fine, dark brown-black suspension. Then 10 g (0.030 mol) of dibromo compound 3 in 2 L of THF was added dropwise, under reflux, to the reduced titanium mixture over a period of 10 h. When the addition was complete, the mixture was refluxed for an additional 30 min. The product mixture analyzed by NMR spectroscopy to determine that no starting material remained and that a 32% yield of product was present. Air was passed through the reaction mixture until the color changed to light yellow, and then the solvent was removed by rotary evaporation. To the residue was added 250 mL of $CHCl_3$, and some solids were filtered. The filtrate was diluted to 750 mL and washed with 5% HCl, saturated $NaHCO_3$ twice, and saturated NaCl solution. The organic layer was then dried ($MgSO_4$), the solvent was removed by rotary evaporation, and the crude product was recrystallized from $CHCl_3$, in the refrigerator overnight to give 1.42 g (27%) of 2: ^1H NMR δ 7.16 ppm (s); ^{19}F NMR ϕ −118.75 ppm (s); ^{13}C NMR δ 129.82 (t, J = 3.4 Hz); MS *m/e* (rel int) 352 (M^+, 18.3), 333 (5.2), 177 (22.1), 176 (100), 126 (20.6), 76 (1.4).

Scheme I



Analogous use of the dichloride as the precursor led to formation of the octafluoro[2.2]paracyclophane in 22% yield.

Isolation of Trimer. The mother liquor from the above recrystallization was evaporated and the residue subjected to column chromatography (silica gel, hexane/EtOAc, 9:1), followed by recrystallization from hexane to give 100 mg (2%) of trimer: ^1H NMR δ 7.33 ppm (s); ^{13}C NMR δ 126.0 ppm (t, J = 4.1 ppm); ^{19}F NMR ϕ −113.87 ppm (s); MS *m/e* (rel int) 528 (91), 509 (10), 478 (7), 352 (4), 333 (14), 314 (12), 301 (8), 176 (100), 126 (43), 76 (2); HRMS gave M^+ 528.0747, calcd for $C_{24}H_{12}F_{12}$ 528.0748.

Preparation of Octafluoro[2.2]paracyclophane (Method B: High Dilution Method). The Ti reducing agent was prepared by adding, over 80 min, 108 mL (108.0 mmol) of 1 M $LiAlH_4$ in 200 mL of THF to 12 mL (108.0 mmol) of $TiCl_4$ in 300 mL of THF, the mixture being stirred under an inert atmosphere and cooled by an ice bath. The same color changes were observed.

About 20% of this Ti* suspension is transferred to a 3-L three-necked flask containing 500 mL of THF and equipped with a reflux condenser, one 500-mL addition funnel containing 10 g (29.8 mmol) of dibromide in 500 mL of THF, and one 500-mL addition funnel containing the rest of the Ti* suspension. The contents of the two addition funnels were added simultaneously, over a period of 10 h and under an inert atmosphere, while the contents of the flask were being refluxed and a stirred using a magnetic stirring bar. When the additions were complete, air was bubbled through the product mixture until the solution clarified. Then $^1/_5$ of the product mixture was evaporated to dryness, $CDCl_3$ added along with a ^{19}F internal standard, and the NMR yield determined to be 38%. The ratio of 2 to trimer was observed to be ca. 7:1.

Isolation of the product and recrystallization as described above gave 1.67 g (31.8%) of 2 and 110 mg (2.1%) of trimer.

***p,p'*-Dimethylbenzoin (8).** The procedure was analogous to that used in the preparation of benzoin.[37] A mixture of 120 g (1 mol) of tolualdehyde and 25 g of KCN in 600 mL of 50% aqueous ethanol was heated at reflux for 2 h. After cooling in an ice bath, the product was filtered, washed with a little cold water, and recrystallized from EtOH to obtain 68.4 g (57%) of product 8: mp 103–105 °C; ^1H NMR δ 2.28 (s, 3 H), 2.34 (s, 3 H), 4.57 (s, 1 H), 5.89 (s, 1 H), 7.09–7.84 ppm (m, 8 H).

***p,p'*-Dimethylbenzil (9).** The procedure was analogous to that used for preparation of benzil.[38] A mixture of 55 g (0.23 mol) of cupric sulfate pentahydrate, 55 g (0.66 mol) of pyridine, and 22 g of water was stirred and heated until solution resulted. To the above solution was added 30 g (0.13 mol) of *p,p'*-

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dimethylbenzoin (8). On pouring into ice water, the product precipitated and was washed with water, dilute HCl, and then water again. Recrystallization from MeOH gave 24.1 g (81%) of **9**: mp 98–100 °C; ^{1}H NMR δ 2.43 (s, 6 H), 7.30 (d, J_{AB} = 8.1 Hz, 4 H), 7.86 (d, J_{AB} = 8.1 Hz, 4 H); ^{13}C NMR δ 21.74 (CH_3), 129.6, 129.9, 130.5, 146.0 (Ar), 194.5 (CO).

***p,p'*-Bis(diacetoxymethyl)benzil (10).** A procedure similar to that of Lieberman and Connor was utilized.[39] A solution of 23.8 g (0.10 mol) of **9** in a mixture of 320 mL of acetic anhydride, 320 mL of acetic acid, and 46 mL of concd H_2SO_4 was cooled to 0–5 °C. Then CrO_3 (56 g, 0.56 mol) was added protionwise over 2 h. The reaction mixture was stirred for one more hour and then was poured into ice. The product was then extracted from the aqueous solution with 5 × 300 mL of ether–CH_3Cl_2(5:1) and washed with water, 5% Na_2CO_3, and water again. Recrystallization from $CHCl_3$ gave 11.8 g (24%) of **10**: mp 110–113 °C; ^{1}H NMR δ 2.15 (s, 12 H), 7.66 (s, 2 H), 8.01 and 7.71 ppm (8 H, AB, J_{AB} = 8.4 Hz); ^{13}C NMR 20.7 (CH_3), 88.7, 127.4, 130.1, 141.9, 141.9, 168.5 ($COCH_3$), 193.2 (CO).

4,4'-Benzildicarboxaldehyde (11). **10** (8.6 g 0.018 mol) in 50 mL of THF and 60 mL of 28% HCl was stirred for 8 h at rt. The product was extracted with CH_2Cl_2, and the organic layer was washed with water, 10% Na_2CO_3, and water. Upon evaporation of CH_2Cl_2 a light yellow solid was obtained which was recrystallized from hexane to give 3.5 g (72%) **11**: mp 180–185 °C; ^{1}H NMR δ 8.17 and 8.05 (AB, J_{AB} = 7.6 Hz, 4 H), 10.15 ppm (s, 1 H); ^{13}C NMR δ 130.0, 130.5, 136.6, 140.2 (Ar), 191.2 (COCO), 192.8 (CHO).

1,2-Bis[4-(difluoromethyl)phenyl]-1,1,2,2-tetrafluoroethane (12). A mixture of 3 g (0.011 mol) of **11**, 12.7 g (0.079 mol) of (diethylamino)sulfur trifluoride (DAST), and 50 mL of dry benzene was stirred at 75 °C for 15 h under N_2. After being cooled to rt, the mixture was poured onto ice and the oil that separated was taken up in CH_2Cl_2 and washed with water, 10% Na_2CO_3, and water again. Recrystallization from hexane gave 3.04 g (76%) of **12**: mp 75–77 °C; ^{1}H NMR δ 6.68 (t, J = 56.2 Hz, 2 H), 7.59 ppm (s, 8 H); ^{13}C NMR δ 109.1, 113.9, 118.7, 125.6, 127.5, 137.2, 133.0 ppm; ^{19}F NMR ϕ −112.1 (s, 4 F), −112.6 (d, J = 56.5 Hz, 4 H); MS *m/e* (rel int) 354 (4.1), 335 (3.6), 178 (7.7), 177 (100), 176 (3.9), 158 (5), 127 (30.8); HRMS gave M^+ 354.0655, calcd for $C_{16}H_{10}F_8$ 354.0655.

1,2-Bis[4-(bromodifluoromethyl)phenyl]-1,1,2,2-tetrafluoroethane (7). A mixture of 2 g (0.0056mol) of **12**, 3 g (0.017 mol) of *N*-bromosuccinimide, and 50 mL of CCl_4 was refluxed and irradiated with UV lamp for 30 h.[40] After filtering the floating succinimide, the CCl_4 solution was washed with water, 10% Na_2CO_3, and water again. The CCl_4 was removed by rotary evaporation, and the product was recrystallized from hexane/$CHCl_3$ (5:1) to give 2.4 g (81%) of **7**: mp 133–135 °C; ^{1}H NMR δ 7.64 and 7.72 (d, J_{AB} = 8.6 Hz); ^{13}C NMR δ 124.4, 127.6, 133.3, 140.8 ppm; ^{19}F NMR ϕ −45.6 (s, 4 F), −111.7 (s, 4 F); MS *m/e* (rel int) 490.7 (2.0), 430.8 (60), 256.9 (30), 177 (15), 176 (100), 126 (25), 107 (5); HRMS gave M^+ 492.8871, calcd for $C_{16}H_8F_8Br_2$ 492.8871.

Acknowledgment. Support of this research, in part, by the Specialty Chemicals Division of Union Carbide Chemicals and Plastics Company is acknowledged with thanks.

Supplementary Material Available: ^{1}H and ^{19}F NMR spectra of compounds **3** (X = Br, Cl), **2**, trimer, **7**, and **12**; ^{1}H and ^{13}C NMR spectra of **9**, **10**, and **11**; and a ^{1}H NMR spectrum of **8** (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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